



Thermal desorption pre-concentrator based system to assess carbon dioxide contamination by benzene

C. Duran^{a,*}, X. Vilanova^b, J. Brezmes^b, E. Llobet^b, X. Correig^b

^a *Department of Electronic Engineering, University of Pamplona, Km 2 Via Bucaramanga, Pamplona, Colombia*

^b *MINOS, Dept. Enginyeria Electrònica, Universitat Rovira i Virgili, Avda. Països Catalans 26, 43007 Tarragona, Spain*

Abstract

A new multisensor system based on a thermal desorption pre-concentrator has been used jointly with a tin oxide gas sensor array to assess the contamination of carbon dioxide by benzene. The results obtained show that using this type of pre-concentrator, it is possible to detect benzene at ppb levels even in the presence of other pollutants at ppm levels.

The system uses a Carbopack B unit that absorbs benzene traces and then releases them concentrated in a factor greater than 200 and is capable of classifying benzene samples down to 10 ppb in a CO₂ flow with different volatile interferences. The e-nose reached a 100% success rate in the classification and identification of the benzene, CO₂ and pollutants. These results show that e-nose technology can be a useful tool as quality control in the beverage industry.

© 2008 Elsevier B.V. All rights reserved.

Keywords: Thermal desorption; Pre-concentrator; Benzene; Gas sensor; Carbon dioxide

1. Introduction

The safety and quality control of food products is becoming a priority issue in developed countries. This means that new and more restrictive legislation is being issued by governments to answer the public awareness of the situation. In the case of gaseous beverages such as sodas and beers, the quality of the CO₂ used is of vital importance to comply with the recommendations of the ISBT (International Society of Beverage Technologists) [1].

The International Society of Beverage Technologists (ISBT) has defined the quality standards for the CO₂ to be used in this application, defining a threshold limit for benzene in 20 ppb, while other hydrocarbons like methane can be present in concentration up to 30 ppm. Metal oxide gas sensors has shown to be candidates for assessing the carbon dioxide quality for these application in low cost equipments to be placed in the beverage production plants [2,3].

Nevertheless the sensitivity to benzene does not accomplish the requirements. So, a pre-concentrator system to increase the

sensors response to benzene has been used in combination with a gas sensor array to extend the measuring range as proposed in [4,5].

To cope with newer legislation requirements, expensive instruments are being used to control CO₂ quality at the production plant [6,7]. Nevertheless, these instruments do not provide on-line analysis and they require specialized personnel to operate them. Moreover, they cannot be used in the transportation of the stage or in the customer plant, phases where the product can be contaminated by external sources.

The work presented in this paper has been developed to address a real need by a CO₂ production plant in Spain. The main goal of the application that will be described is devoted to the detection of benzene down to the values recommended by the ISBT (around 5–10 ppb) in a CO₂ flow with a 99.95% purity level. Even at this purity value, many interfering volatiles can still be found, as described in Table 1. These requirements should be achieved with a cheap and reliable system that could be easily installed, operated and maintained at the customer facilities or even embedded in the transportation system.

To achieve such ambitious goals a carefully devised research and development effort has been planned. The first stage of such a plan is to design a prototype to evaluate the feasibility of the approach selected. For the first time, a prototype based on a semi-

* Corresponding author.

E-mail address: cmduran@unipamplona.edu.co (C. Duran).

Table 1
Typical contaminants with their maximum concentrations allowed in 99.95% purity CO₂

Pollutant	Maximum concentration allowed
Water (ppm)	8
Total aldehydes (ppb)	200
Ammonia (ppm)	2
Benzene (ppb)	20
Nitrogen dioxide (ppb)	500
Sulfide dioxide (ppm)	2
Heavy hydrocarbons (ppm)	1
Volatile hydrocarbons (ppm)	20
Methane (ppm)	30
Carbon monoxide (ppm)	2
Nitrogen (ppm)	40
Nitric oxide (ppm)	2.5
Oxygen (ppm)	9
Hydrogen sulphide (ppb)	500

Bold value indicates the principal pollutant of investigation in the work.

conductor multisensor array coupled to a thermal desorption unit has been proposed to detect benzene under a CO₂ flow.

The coupling of thermal desorption units to multisensor systems based on semiconductor gas sensors to enhance their sensibility has been proposed before [8–15]. Anyhow, these systems have never been used under a CO₂ atmosphere, since the general belief that tin oxide gas sensors need oxygen to interact have prevented their use in this type of applications. Nevertheless, recent publications prove that these types of sensors perform in a similar way under a CO₂ atmosphere. Moreover, in the prototype designed a novel and simple made-in-house design has been proposed and tested for the thermal desorption unit.

This paper has been organized in four different sections. The second chapter describes the experimental of the prototype fabricated, including the design process followed until the definitive prototype has been completed. Section 3 describes the results obtained and discusses the suitability of the instrument designed to the application sought. Finally, Section 4 outlines the conclusions of our work.

2. Experimental

2.1. General configuration

The system initially proposed consists of four different electro-valves, a platform with the thermal desorption unit, a sensor chamber, electronic circuitry and a personal computer system to control the measurement process, acquire sensor signals and to process those signals into useful information. Fig. 1 shows the configuration proposed.

The measurement process starts when electro-valves 1 and 4 redirect the CO₂ flow to the adsorption system as the dashed line illustrates. In this configuration, benzene impurities are absorbed in the carbon powder during a predefined period of time. Once the concentration phase is finished, the thermal desorption phase can be activated using the same circuit or in the other direction, changing the position of electro-valves 2 and 3. Electro-valve 5 has been included to maintain the same flow in the sensor chamber no matter the measurement phase.

The sensor chamber houses a minimum amount of sensors (4 units) in order to minimize the dead volume of the system and the energy consumption. A software controls the measurement process in real-time so that the system completes each measurement in the same way in order to obtain a repetitive set of measurements.

2.2. Sensor array design and optimisation

Two different sensor chambers were designed for the system. The first chamber (seen in Fig. 2) was specifically designed to determine which sensors were going to be housed in the final prototype. With that goal in mind, the chamber was capable of housing up to 15 sensors at the same time.

Using the first chamber, measurements were performed to determine the sensitivities of 21 different sensors against benzene. Table 2 describes the sensors tested. In order to be sure about which sensors were more sensitive to benzene, concentrations of 20, 7, 5 and 2 ppm were measured with all 22 sensors. Table 3 describes the sensors chosen after determin-

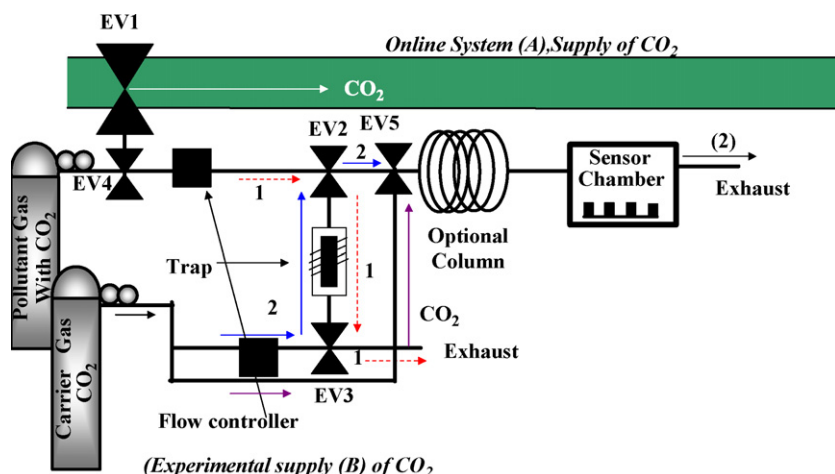


Fig. 1. Plant of the prototype.

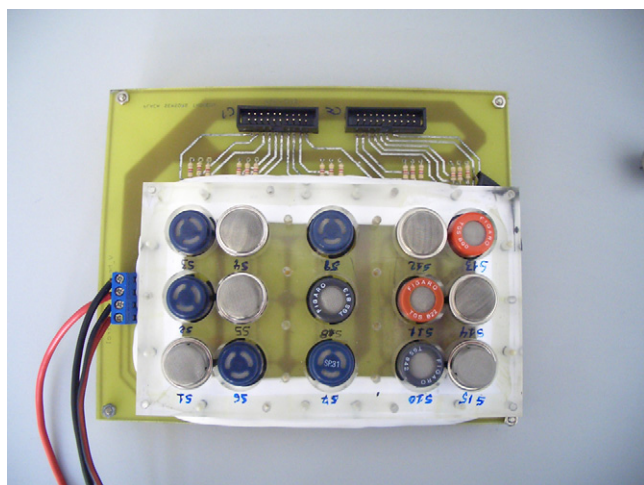


Fig. 2. Sensor chamber, capacity 15 commercial sensors (FIS and Taguchi TGS).

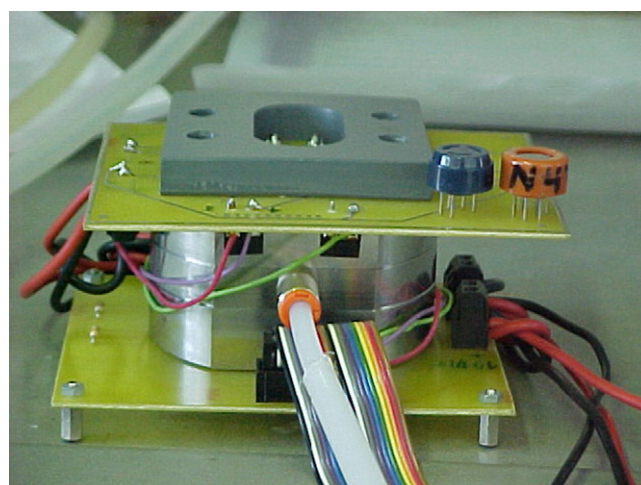


Fig. 3. Sensor chamber fabricated with dead volume.

Table 2
Metal oxide sensors

Amount	Type	Application
	Taguchi (series-8)	
1	TGS-800	Air quality, smoke, benzene
2	TGS-821	Hydrogen
1	TGS-880	Nourishing product scents
1	TGS-813	Combustible gas
1	TGS-842	Methane, natural gas
2	TGS-822	Organic solvents
2	TGS-823	Organic solvents (benzene)
2	TGS-826	Ammoniac
	FIS (series-SP)	
2	SP-MW0	General intention; kitchen control.
2	SP-11-00	General purpose; inflammable steam
2	SP-53	Hydrocarbons
2	SP-AQ2-00	Air quality, VOC's
2	SP-AQ3-00	Combustible gas

ing the best sensitivities (defined as the normalized conductance increment).

The final chamber housed the four most sensitive sensors against benzene. Fig. 3 shows how the chamber was fabricated; it is made in stainless steel and sufficiently robust for the application. The three pieces that form are symmetrical, and they are fixed with others with screws for which make a pressure the one on the other. The dead volume was minimized to 0.6 ml with external dimensions of 10 mm × 10 mm × 6 mm.

Table 3
Sensors chosen after determining the best sensitivities (defined as the normalized conductance increment)

Sensor	Normalized conductance $(C_{max} - C_i)/C_i$
TGS 800	0.6011
TGS 822	0.7648
TGS 823	1.3995
SP 31	1.4926

2.3. Design and fabrication of the thermal desorption unit

The thermal desorption unit envisaged for the system had to comply with three different features:

- High temperature heating, up to 350 °C, since carbon concentrators need a temperature higher than 300 °C to be activated and to be cleaned completely.
- Low thermal inertia to be able to ramp up temperature as fast and accurate as possible.
- Easy coupling of temperature proves to accurately monitor heating temperature.

Different systems were proposed and carefully evaluated. Fig. 4 shows a schematic diagram of the approach chosen in the end. For this system a heating wire (Inc. Engineering Omega) and glass tube (Borosilicate) were used in the application. The filament of 0.50 mm diameter is made of nickel–chromium, which is used in applications with high temperatures, for example furnaces and radiators. These wires can reach temperatures over 1000 °C.

Table 4 shows the temperatures and transient times achieved by this system. Fig. 5 shows a real picture of the device constructed. Table 5 shows the characteristics of this material. Temperature was controlled using a k-type thermocouple. Fig. 6 shows the electronic circuit connected to the thermocouple used.

Table 4
Temperatures and transient times achieved by thermal desorption unit

# Test	Current (A)	100 °C (s)	150 °C (s)	200 °C (s)	250 °C (s)
1	4.40	1.5	2.55	5.5	6.5
2	4.43	1.5	2.5	5.2	6.3
3	4.45	1.2	2.3	5	6
4	4.45	1.2	2.2	5	6
5	4.50	1	2	4	5
6	4.55	1	2	4	5

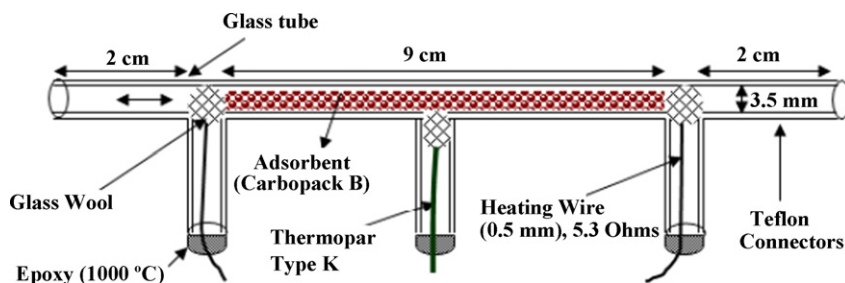


Fig. 4. Schematic diagram of the approach chosen in the end.

The tube was filled with Carbopack B adsorbent. An amount of 400 mg adsorbent was used, located internally in the glass tube, with 15 cm (9 cm for the adsorbent one) length, 7 mm of external diameter and 3.65 mm of internal diameter. Two fiber

glass corks of 5 mm each one were located in each one of the ends of the tube with the objective to avoid that the charcoals moved to the outside due to the gas flow. The total volume of the tube was of 0.86 ml (cm³).

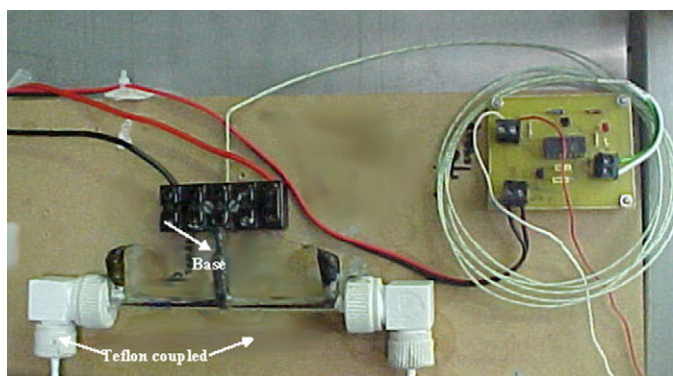


Fig. 5. Thermal desorption unit constructed.

2.4. System automation

In order to obtain repetitive results, the whole measurement process had to be automated. In fact, the automation of the equipment was one of the initial premises that had to be proved if the system ever becomes commercially available. A PC was in charge of the measuring process, controlling the following devices:

- All the electro-valves
- A current controlled source, with a maximum amperage of 4 A
- The sensor chamber

Fig. 7 shows the final system configuration with the different subsystems. Different lines show the different pathways that could be used. One possibility is to use the solid line for both absorption and desorption. A second possibility is to use the dashed line for absorption and the solid line for desorption.

Table 5
Characteristics of the material

Adsorbent	Carbopack B
Mesh	60/80
Surface area (m ² /g)	100
Density (g/ml)	0.36
Application	C ₅ -C ₁₂

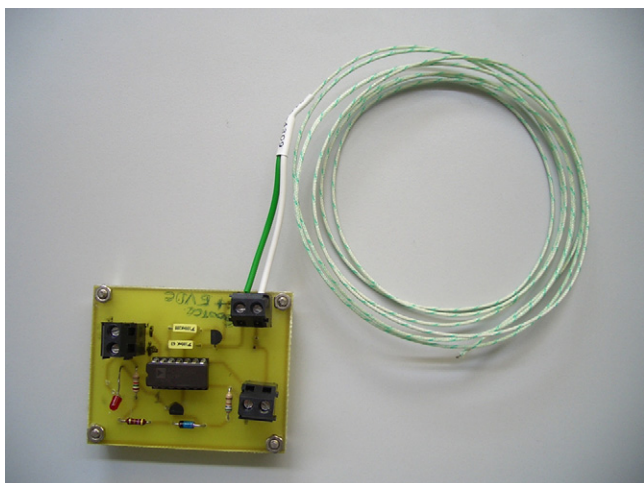


Fig. 6. Control circuit (thermopar type k).

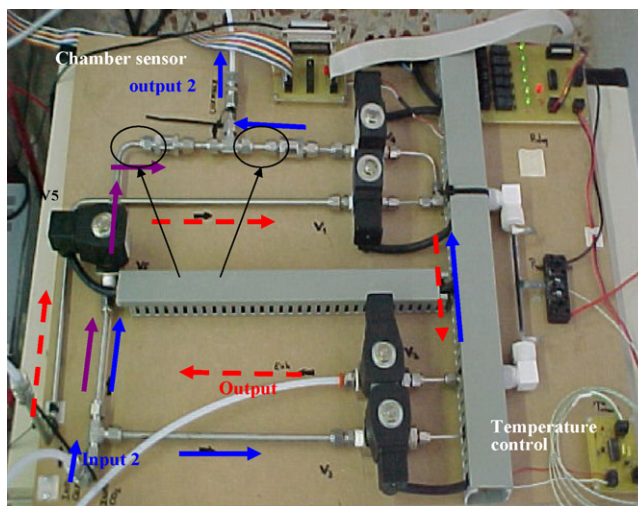


Fig. 7. The final system configuration with the different subsystems.

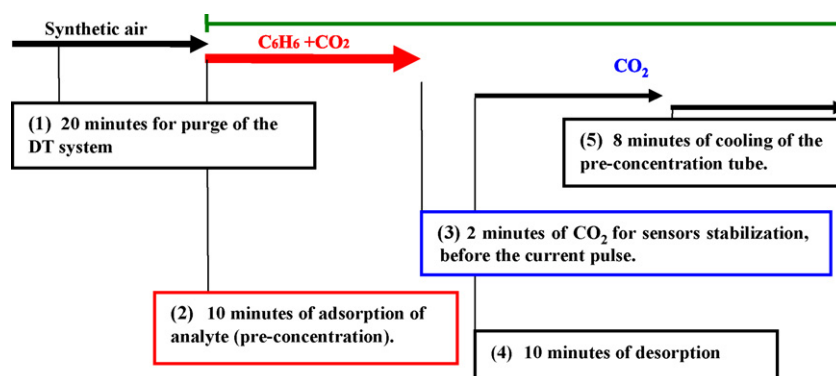


Fig. 8. Chronogram of the measurements made with the prototype.

3. Results and discussion

3.1. Experimental design

Fig. 8 shows the chronogram of the measurements made with the prototype. Initially, synthetic dry air cleans the adsorbent during 20 min, to make sure there are no rests from previous measurements. After that, contaminated CO₂ (with a given concentration of benzene) was directed through in the adsorption tube during 10 min. After those 10 min, a flow of CO₂ was applied during 2 min to stabilize the sensor response before applying the current to heat the adsorbent, which lasted ten additional minutes. After that, 8 additional minutes were used to cool the system.

With this approach, 200 °C was reached during the desorption phase and 25 °C after the cooling period. In most of the cases a second desorption cycle was performed in order to assure the complete desorption of the benzene. Fig. 9 shows the sensor array response to three consecutive desorptions. It can be seen that after the first desorption cycle, the second and third bear no sensor response, assuring that the first one desorbed completely the benzene concentrated.

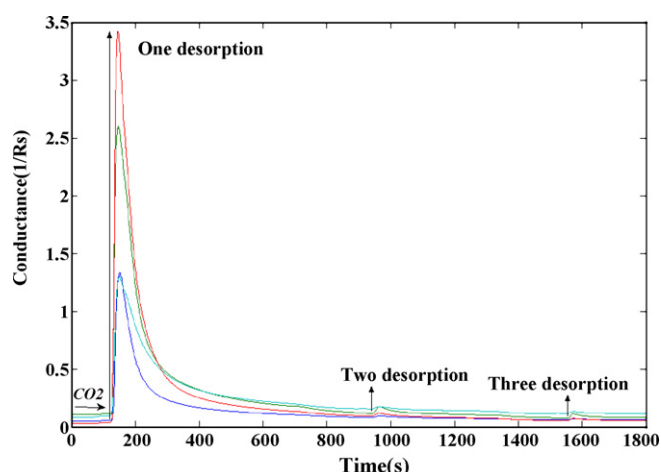


Fig. 9. Sensor array response to three consecutive desorptions.

3.2. Measurements

A set of 65 measurements were performed, and obtained with adsorptions of 150, 70, 20 and 10 ppb of benzene under a CO₂ flow. Tables 6–8 shows the different mixtures measured with 10 ppb and 20 ppb of benzene and their codification, where it can be seen that clean CO₂ and CO₂ plus other interferences were also included in the measurement set to classification.

The gas sensor electrical conductance has been monitored and acquired. The information processed has the maximum value of conductance during the desorption process.

Table 6
Different mixtures measured with 20 ppb of benzene

Compound	Mixture
20 ppb benzene (C ₆ H ₆) + 5 ppm methane (CH ₄) + 2 ppm CH ₃ OH (methanol + CO ₂)	A
20 ppb benzene + 25 ppm methane (CH ₄) + 10 ppm CO + CO ₂	B
CO ₂ C-45	C
20 ppb benzene (C ₆ H ₆) + CO ₂	D
0.1 ppm SO ₂ + CO ₂	E
E + 20 ppb benzene + CO ₂	F
25 ppm methane (CH ₄) + 10 ppm CO + CO ₂	G
G + 20 ppb of benzene + CO ₂	H
5 ppm of methane + 2 ppm methanol + CO ₂	I
I + 20 ppb of benzene + CO ₂	J
4 ppm methanol + CO ₂	K
K + 20 ppb of benzene + CO ₂	L
1.5 ppm (argon + O ₂) + CO ₂	M
M + 20 ppb benzene + CO ₂	N

Table 7
Different mixtures measured with 10 ppb of benzene

Compound	Mixture
CO ₂ C-45	1
10 ppb benzene + 4 ppm of methanol + CO ₂	2
10 ppb benzene + 5 ppm methane (CH ₄) and 2 ppm methanol + CO ₂	3
10 ppb benzene + 25 ppm methane (CH ₄) + 10 ppm CO + CO ₂	4
10 ppb benzene (C ₆ H ₆) + 0.1 ppm of SO ₂ + CO ₂	5
10 ppb benzene (C ₆ H ₆) + CO ₂	6
10 ppb + 1.5 ppm of O ₂ + argon + CO ₂	7

Table 8
 Different mixtures measured and their codification to classification

# Measurement	Compound	Codification
24	20 ppb of benzene + interferences + CO ₂	20
18	10 ppb of benzene + interferences + CO ₂	10
15	Interferences + CO ₂	IN
8	CO ₂	C

3.3. Results

Figs. 10 and 11 shows two PCA graph were it can be seen the different clusters corresponding to different types of measurements.

It is clear that the system devised is able to discriminate measurements with as low as 10 ppb compared to pure CO₂ or CO₂ with other interfering species.

A fuzzy artmap neural network was applied with a leave-one-out approach to see how well a neural network could distinguish between the different situations. Tables 9 and 10 show the results considering a classification comprising all the species, a categorization between 20 ppb, 10 ppb and no benzene samples and presence/absence of benzene.

From the results it is clear that the system is capable of detection reliably up to 10 ppb of benzene despite the presence of other interferences gas. With these results we have evaluated the capacity to detect 10 ppb of benzene in a flow of CO₂ connecting an electronic nose to a stage of thermal desorption. In the end,

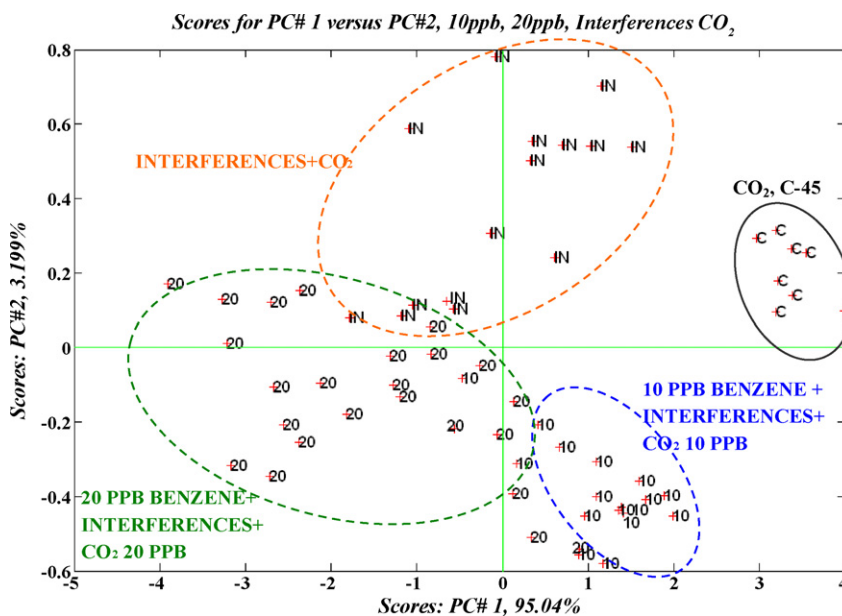


Fig. 10. PCA graph with different types of cluster (10 ppb, 20 ppb, interferences and CO₂).

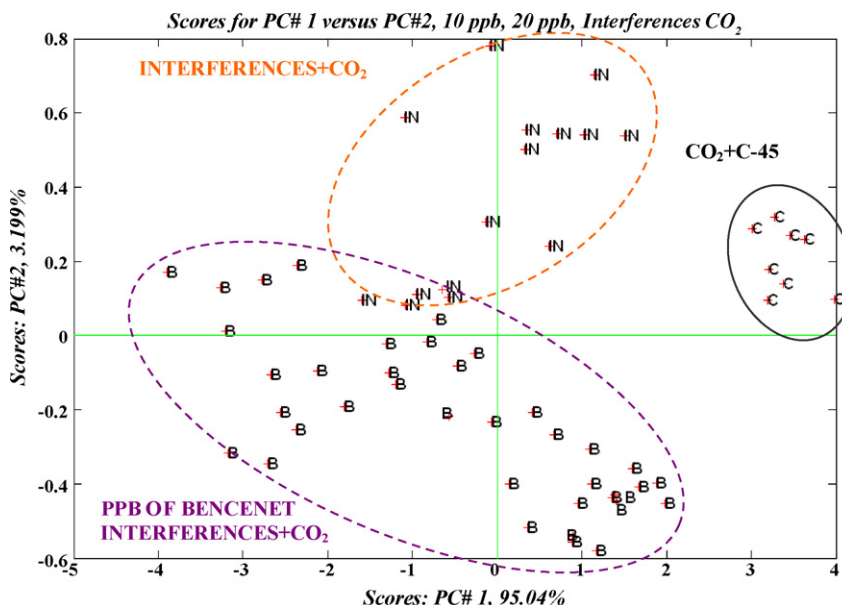


Fig. 11. PCA graph with different types of cluster (10 ppb with 20 ppb, interferences and CO₂).

Table 9
Classification with four categories (10 ppb, 20 ppb, interferences and CO₂ pure)

Normalization method	Success rate with the fuzzy ARTMAP (%)
Auto-scaled	89
Mean-centring	84
Matrix normalization	89
Sensor normalization	87

Table 10
Classification with three categories (10 ppb with 20 ppb, interferences and CO₂ pure)

Normalization method	Success rate with the fuzzy ARTMAP (%)
Auto-scaled	97
Mean-centring	92
Matrix normalization	95
Sensor normalization	94

the detection of benzene in a CO₂ flow was of 97% success rate using the normalization method “Auto-scaled”.

4. Conclusions

The results obtained in this work show that is possible to determine contamination of carbon dioxide by benzene at trace levels even in the presence of other pollutants at ppm levels combining a pre-concentrator and a gas sensor array. Nevertheless, the system in the present form does not allow to determine the benzene concentration.

We have demonstrated how a multisensor system based on semiconductor gas sensors is able to detect down to 10 ppb of benzene under a CO₂ atmosphere despite the presence of other contaminant species. The use of a cheap made-in-house thermal desorption unit has the potential to boost sensitivity between 100 and 500 times the one showed by the sensor system alone, making the detection of ppb traces of benzene possible in such application.

Acknowledgment

This work has been supported by S.E “Carburos Metálicos” of Barcelona (Spain).

References

- [1] ISBT carbon dioxide quality guidelines and analytical procedure bibliography, International Society of Beverage Technologists, USA, March 2001.
- [2] X. Vilanova, X. Correig, E. Llobet, J. Brezmes, X. Sanchez, R. Calavia, Carrier gas analyzer detecting reducing and oxidizing gases includes metal oxide based sensors with graphical representation of the measurements, Patent number ES2212739-A1, PATENT 2004.
- [3] X. Vilanova, E. Llobet, J. Brezmes, R. Calavia, X. Sanchez, X. Correig, A multisensor system for monitoring the quality of carbon dioxide in the beverage industry, in: *Transducers'03: Digest of Technical Papers*, vols. 1 and 2, International Society of Beverage Technologists, Boston, USA, March, 2001, pp. 1347–1350.

- [4] C.E. Davis, C.K. Ho, R.C. Hughes, M.L. Thomas, Enhanced detection of *m*-xylene using a preconcentrator with a chemiresistor sensor, *Sens. Actuators B* 104 (2005) 207–2164.
- [5] L.C. Jung, T.Z. Edward, A dual-adsorbent preconcentrator for a portable indoor-VOC microsensor system, *Anal. Chem.* 73 (2001) 3449–3457.
- [6] R.L. Firor, B.D. Quimby, Analysis of Trace Sulfur Compounds in Beverage Grade Carbon Dioxide, Agilent Technologies Inc., USA, 2001, April 2.
- [7] Trace impurities in beverage-grade CO₂ incorporating the amperometric sulfur detector. PerkinElmer, Inc., USA, <http://www.perkinelmer.com/>, 2005.
- [8] Leonello Dori, et al., A Gas Chromatographic-like System for the Separation and Monitoring of Benzene Toluene and Xylene Compounds at the ppb Level Using Solid State Metal Oxide Gas Sensors, Instituto di Scienze Chimiche “F. Bruner”, University of Urbino, Italy, 2000.
- [9] T. Rechenbach, et al., Improvement of the sensitivity of an ammonia gas sensor based on a quartz microbalance by thermal desorption, in: *The 13th European Conference on Solid-State Transducers (Euroensors XIII)*, September 12–15, The Hague, The Netherlands, 1999, pp. 705–708.
- [10] F. Bender, N. Barié, G. Romoudis, A. Voigt, M. Rapp, Development of a preconcentration unit for a SAW sensor micro array and its use for indoor air quality monitoring, *Sens. Actuators B* 93 (2003) 135–141.
- [11] H. Tim, J. Niess, P.L. Schulze, B. Diekmann, P. Boeker, Online measurement of odorous gases close to the odour threshold with a QMB sensor system with an integrated preconcentration unit, *Sens. Actuators B* 95 (2003) 39–45.
- [12] Q.Y. Cai, J. Park, D. Heldsinger, M.-D. Hsieh, E.T. Zellers, Vapor recognition with an integrated array of polymer-coated flexural plate wave sensors, *Sens. Actuators B* 62 (2000) 121–130.
- [13] E.T. Zellers, M. Morishita, Q.-Y. Cai, Evaluating porous-layer opentubular capillaries in a microanalytical system, *Sens. Actuators B* 67 (2000) 244–253.
- [14] N. Johannes, H. Tim, S.L. Peter, W. Edwin, B. Peter, A miniaturized thermal desorption unit for chemical sensing below odor threshold, *Sens. Actuators B* 95 (2003).
- [15] W. Muenchmeyer, A. Walte, G. Matz, Improving electronic noses using a trap and thermal desorption unit, *Sens. Actuators B* 69 (2000) 379–383.

Biographies

Cristhian Durán, graduated in Electronic engineering from the Pamplona University, Pamplona, Colombia, in 2000, and received his PhD from the Universitat Rovira I Virgili, Tarragona, Spain, in 2005. He is currently an Professor in the Electronic Engineering Department, Pamplona University, Pamplona (N.S.) Colombia. His main areas of interest are in Automation and Control and applications with chemical sensor arrays for complex aroma analysis through signal processing techniques, such as neural networks.

Xavier Vilanova, graduated in telecommunication engineering from the Universitat Politècnica de Catalunya (UPC), (Barcelona, Spain) in 1991, and received his PhD in 1998 from the same university. He is currently an associate professor in the Electronic Engineering Department at the Universitat Rovira I Virgili (Tarragona, Spain). His research activities are related to semiconductor gas sensors development and characterisation, as well as, gas sensors systems design.

Jesús Brezmes, graduated in telecommunication engineering from the Universitat Politècnica de Catalunya (UPC) (Barcelona, Spain) in 1993. He received his PhD in 2001 from the same university. He is currently an associate professor in the Electronic Engineering Department at the Universitat Rovira I Virgili (Tarragona, Spain). His main area of interest is in the application of signal processing techniques such as neural networks to chemical sensor arrays for complex aroma analysis.

Eduard Llobet, graduated in telecommunication engineering from the Universitat Politècnica de Catalunya (UPC), (Barcelona, Spain) in 1991, and received his PhD in 1997 from the same university. He is currently an associate professor in the Electronic Engineering Department at the Universitat Rovira I Virgili (Tarragona, Spain). His main areas of interest are in the fabrication, and modeling

of semiconductor chemical sensors and in the application of intelligent systems to complex odour analysis. Dr. Llobet is a senior member of the IEEE.

Xavier Correig, graduated in telecommunication engineering from the Universitat Politècnica de Catalunya (UPC), (Barcelona, Spain) in 1984, and received

his PhD in 1988 from the same university. He is a full professor of electronic technology in the Electronic Engineering Department at the Universitat Rovira I Virgili (Tarragona, Spain). His research interests include heterojunction semiconductor devices and solid-state gas sensors.